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Supporting Material for

Direct observation of increasing CO₂ in the Weddell Gyre along the Prime

Meridian during 1973-2008

by

Steven van Heuven^{a*}, Mario Hoppema^b, Oliver Huhn^c, Hans Slagter^a, Hein de Baar^{a,d}

This supplement contains additional details pertaining to the analytical procedures followed during the measurements of C_T , A_T , O_2 and dissolved nutrients during expedition ANT-XXIV/3 of the R/V Polarstern. These additional details are presented in the form of excerpts from i) the post-cruise report of the processing of the C_T and A_T measurements (full details available on request) and ii) the cruise report of this expedition, for O_2 and dissolved nutrients.

ANT-XXIV/3 Carbon Measurements

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The Netherlands

October 31st, 2008

1 Metadata

Name of cruise: ANTXXIV/3

Research vessel: F/S Polarstern

Time: Feb 10th (Cape Town, South Africa) to April 16th 2008 (Punto Arenas, Chili)

Working area: Prime Meridian, Weddell Sea, Drake Passage

Parameters: Total alkalinity (TALK) and dissolved inorganic carbon (DIC)

Analyst: Steven van Heuven and Hans Slagter (RuG)

Analyzer: VINDTA's #17 ('A') and #15 ('B') (NIOZ)

Data processing: Steven van Heuven (RuG)

Samples analyzed: 2402 + 2350 (of which 60% oceanographic samples)

CRM analyses: 101 + 100 (mostly batch 86)

2 Analytical methods

2.1 Analyzer description

Samples were analyzed on two VINDTA 3C's (Versatile Instrument for Determination of Titration Alkalinity), developed and built by Dr. Ludger Mintrop, MARIANDA, Kiel, Germany. These devices concurrently perform a potentiometric alkalinity titration and a coulometric DIC titration (see DOE1994 and references therein). Calculations performed by the VINDTAs at time of measurement were considered to be preliminary, because of a lack of accurate salinity and nutrient values which are required for these calculations. Storage of all raw titration results allowed for post-cruise recalculation of all results.

2.2 Sampling procedure

Samples were collected in 500ml borosilicate bottles following 'the DOE handbook' (Dickson and Goyet, 1994), except they were not poisoned with HgCl₂, and plastic rather than glass stoppers were used. Samples were stored dark, with rubber bands around the stoppers and in styrofoam packaging for thermal insulation, until analysis - which was generally within 2-12 hours. Headspace equilibration correction (ΔD) was not performed, because the atmospheric concentration of CO₂ in the rosette tapping room was not known. Since headspace volume was consistently very low ($\sim 1\%$ of sample volume), no influence on DIC of more than $.5 \mu\text{mol/kg}$ is expected. Samples from a particular station were generally not divided

of the two analyzers, but rather ran on one of both machines. Occasionally, samples were analyzed on both machines concurrently (the large sample volume allows this), which allows for machine-to-machine comparison.

2.3 Analysis procedure

Sample bottle stoppers were removed immediately prior to insertion of the sample line to the machine. Samples were ‘injected’ into the VINDTA by creating an over-pressure of ~ 0.5 bar in a sample’s headspace using air from the ship’s central compressed air circuit. Injection was through a counter-flow heat-exchange system that brought a sample’s temperature up to within of 0.1°C of analysis temperature (25°C), irrespective of a sample’s initial temperature. This procedure allows for convenient sample handling and constant analysis temperature. Further temperature equilibration was assumed to take place in the pipettes, where the samples was allowed to stand for 30 seconds before dispensing into the TAlk titration cell or the DIC stripper. Due to the over-pressure system, no excessive bubble formation (dissolved gas coming out of solution) was observed. Sample was first used to rinse and fill the DIC pipette, and after that to rinse and fill the TAlk pipette. Care was taken to avoid sample carry-over (by separating subsequent samples by a small volume of air). In order to set the measurement accuracy, Certified Reference Material (made available by prof. A. Dickson, SIO, USA) was analyzed at least three times per day, but never before both the coulometric cells were successfully started (i.e., after a suitable number of dummy runs were performed and coulometer blank level was stable). To be able to track the response of the VINDTA with a higher temporal resolution, ‘labstandards’ were analyzed approximately every two hours. These labstandards were prepared on board in batches of $\sim 60\text{L}$, using water from deeper than 1500m , which was filtered, poisoned with HgCl_2 and brought to lab- and analysis temperature (25°C). The vessel of labstandard was placed under continuous overpressure of ~ 0.5 bar. Before pressurization, the labstandard was sparged with lab-air to attain a pCO_2 that was expected to approximate the pCO_2 that the pressurized headspace was expected to attain (i.e., 1.5 times the ship’s compressed air pCO_2). A manifold (placed before the heat-exchanger) allowed the analyst to easily switch from analyzing ‘bottle-contained’ samples to labstandards and back. Measurements were performed around the clock with only minimal downtime during cell replacement and restart (circa once a day, two hours per machine).

Accurate determination of pipette volumes has been performed by post-cruise weighting of in-cruise dispensed volumes of distilled water. Results are accurate to better than 1 in 4000 for DIC (i.e., $\sim 0.5\mu\text{mol/kg}$), and 1 in 1500 (i.e., $\sim 1.5\mu\text{mol/kg}$) or TAlk (using different scales, both more accurate than attained results). Pipette volumes are assumed to have remained constant during the cruise.

2.4 DIC-specific remarks

DIC determinations were performed using the standard coulometric method, using two UIC coulometers (one model 5011, one model 5012). No electronic calibration has been performed either pre- or post-cruise, and an inaccuracy may be present in the coulometric data up to 1% (i.e., $20\mu\text{mol/kg}$) in either direction. This error is expected to have been very constant during the course of the expedition, to have a linear effect on the measured values and therefore to be exactly correctable through the use of CRM. No gas-loop calibration was used. No coulometric cell thermostating was performed.

2.5 TAlk-specific remarks

TAlk determinations were performed by an acid titration that combines aspects from both the commonly used ‘closed cell’ method and the ‘open cell’ method, following the VINDTAs standard settings. A single 20L batch (#1) of acid of $\sim 0.1\text{M}$ (and salinity 35) was prepared to be used by both VINDTAs. On March 12^{th} , when less than $\sim 10\text{L}$ of acid remained, this remainder was used solely by VINDTA B whereas a new 20L batch (#2) was prepared for VINDTA A. On March 25^{th} (i.e., two weeks after the new acid was prepared, and seven weeks after the initial batch was made), the strengths of the two batches were determined on board to be $0.1036 \pm 0.0005\text{M}$ (batch #1) and $0.1062 \pm 0.0010\text{M}$ (batch #2). Potential drift in acid strength due to HCl -gas loss to acid vessel headspace is not accounted for.

New electrodes from Metrohm (reference) and Orion (measurement) were used, but no formal assessment of their quality (E^0 , Nernst response) was performed. However, when TAlk measurement quality

began worsening significantly on machine B, several spare electrodes were tried, with no resulting improvement.

Halfway the cruise, a series of CRM's of different batches was run on both machines. The range of values analyzed confirmed the excellent linearity and low intercept (i.e., the 'calibration curve' is linear through zero) of the DIC measurements (see figures 5 and 6). TAlk measurements are excellently linear as well, but on each machine show an unexplained, non-significant intercept and below-1 slope.

3 Analytical quality assessment

This section briefly discusses some of the measurement quality indicators displayed in the figures below. By no means should this be considered an exhaustive quality assessment. Study the figures for a more thorough understanding if so desired. The terms 'corrected' and 'uncorrected' refer to the mathematical adjustment of results to agree with CRM results.

3.1 Initial measurement accuracy:

As can be seen from figures [1 2 3 4], uncorrected CRM measurements for DIC were less than 1% offset from certified values. The drift trough time of VINDTA's responses are responsible for part of the spread observed in the histograms. The significant offset of VINDTA B is believed to result from bad electronic calibration of its coulometer. TAlk values are about 0.5-1% low for both machines (expected to result from inaccurate calibration of titration acid, which apparently was slightly stronger than determined), with machine B displaying much higher variability than A. This variability is partly stochastic, partly resulting from time drift.

3.2 Measurement precision

Short term replicability: Both field- and analytical replicates were performed during the cruise. Of each set of such replicates that was analyzed back-to-back (i.e., one immediately following the other), the difference between the two samples is shown in figures 9 and 10. Short term repeatability is thus $\sim 1.4 \mu\text{mol/kg}$ for DIC for both machines and $\sim 2.2 \mu\text{mol/kg}$ for TAlk. Non-zero average offsets between each two runs may be indicative of either gas exchange between sample and headspace (in case of DIC analytical replicates) or (in the case of DIC field replicates or TAlk replicates), of very slight carryover between the first replicate and the sample before it.

3.3 Correction results

A comparison of initial (=uncorrected) detrended normalized labstandard results with the final (=corrected) detrended normalized labstandard results, shows a significant improvement for DIC (VINDTA A: $2200.0 \pm 3.0 \mu\text{mol/kg}$ becomes $2200.0 \pm 2.0 \mu\text{mol/kg}$, VINDTA B: $2200.0 \pm 3.0 \mu\text{mol/kg}$ becomes $2200.0 \pm 2.3 \mu\text{mol/kg}$) (no figure), indicating that at least part of the variability observed in DIC CRM results is reflecting varying VINDTA response, and is successfully corrected for.

For TAlk, the results are not as convincing: (VINDTA A: $2400.0 \pm 2.0 \mu\text{mol/kg}$ remains $2400.0 \pm 2.0 \mu\text{mol/kg}$, VINDTA B: $2400.0 \pm 3.8 \mu\text{mol/kg}$ becomes $2400.0 \pm 3.5 \mu\text{mol/kg}$) (no figure). Spread on VINDTA A was already very low, and no improvement is observed by the whole procedure followed. VINDTA B's results are somewhat improved, but remain noisy.

3.4 Machine inter-comparability

When a sample was analyzed on two machines at the same time, the values obtained from both machines are expected to match each other very closely - especially after correction to CRMs. In figure 13 it can be seen that this is definitely the case for DIC measurements, featuring an excellently low offset of $\pm 0.1 \mu\text{mol/kg}$ (keep in mind that the two dataset are acquired and processed fully independently!) and a spread as low as $\pm 2.1 \mu\text{mol/kg}$. Only a dozen or so samples can be observed to have machine-to-machine differences of more than $5 \mu\text{mol/kg}$. These samples have been flagged as questionable in the final dataset.

For TAlk, however, the results are vastly different. A very large spread is visible, the worst (left-) tail of which results from strong deterioration of VINDTA B's TAlk measurements from March 24th

onwards. When excluding that data (no figure), the spread decreases to $\pm 3.0 \mu\text{mol/kg}$, but the offset of $\sim 5 \mu\text{mol/kg}$ becomes even clearer. The cause of this offset is not confirmed, but likely stems from use of a bad measurement electrode on machine B. Clearly, the TALK values of the two machines may not simply be averaged and included in the cruise's final dataset. VINDTA B's TALK data are discarded, based on its generally lesser quality results (TALK RMS, labstandard spread, CRM drift, etc.), although the first two thirds of that data may very well be salvageable. All TALK data obtained by machine B are flagged as questionable in the final dataset, and 'mean' TALK values for the cruise are identical to machine A's.

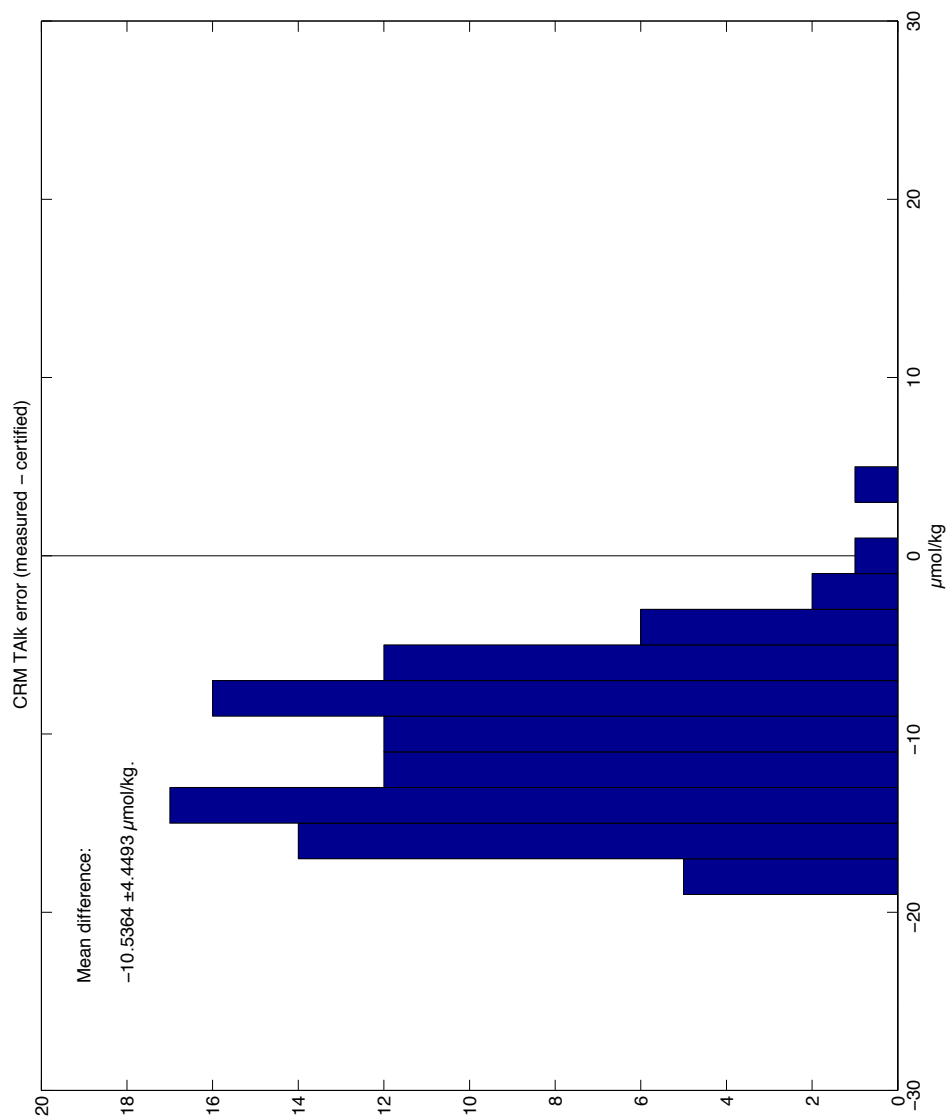


Figure 1: Difference between measured and certified TALK values of measured CRMs, VINDTA A.

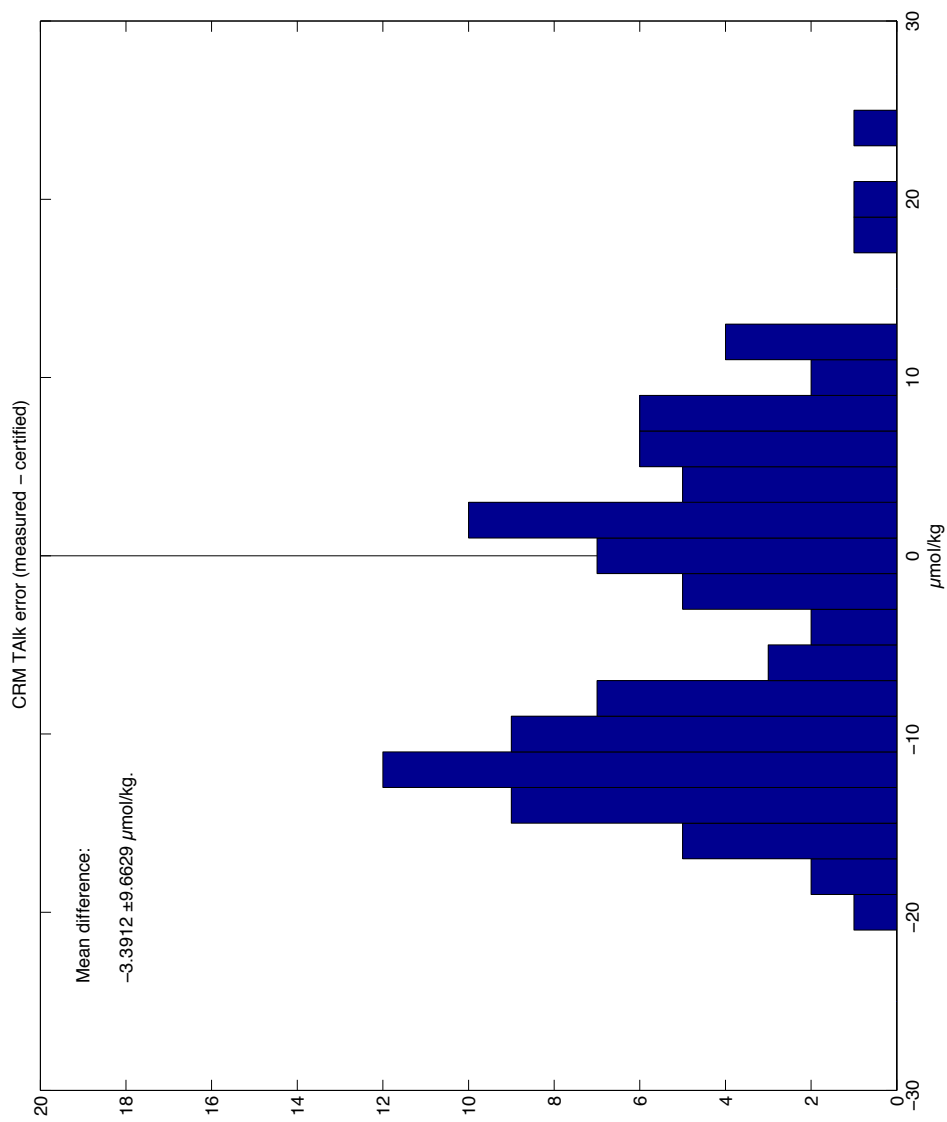


Figure 2: Difference between measured and certified TALK values of measured CRMs, VINDTA B.

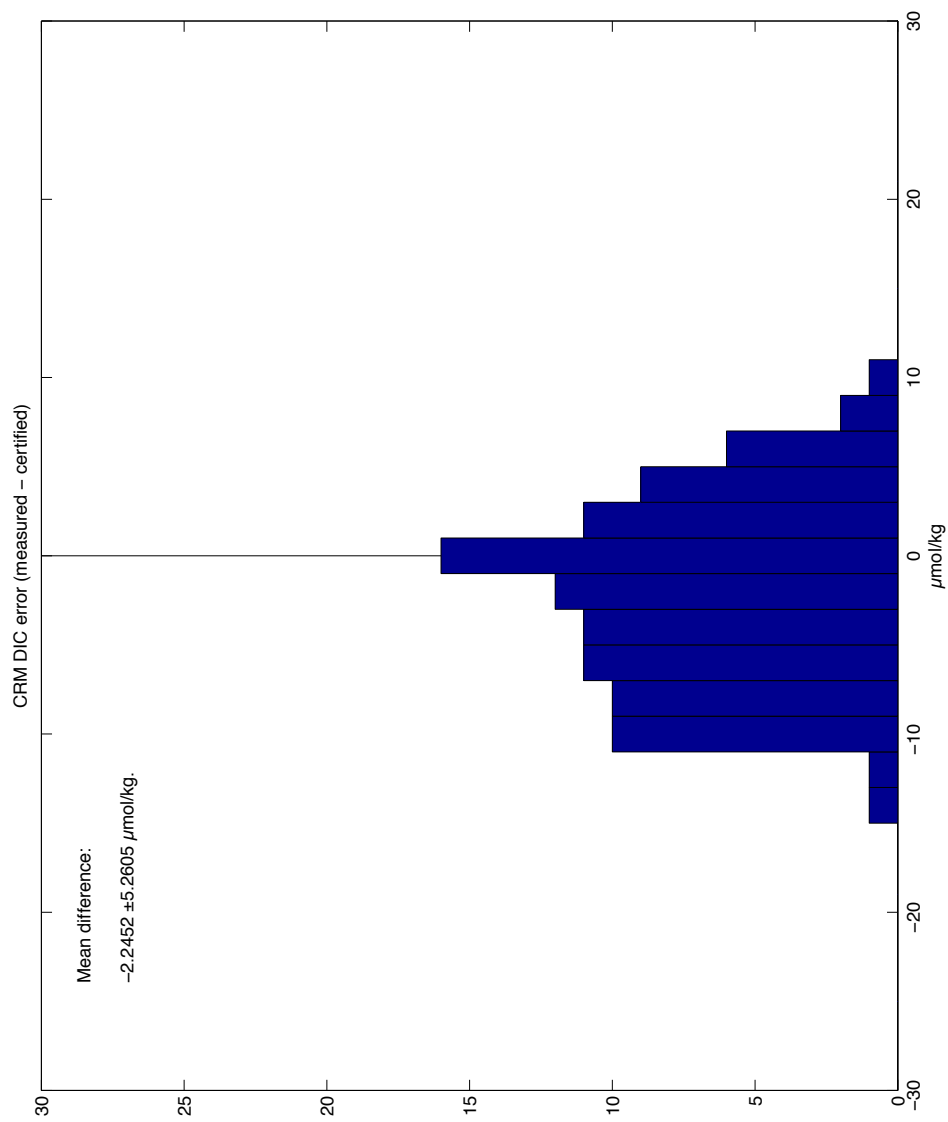


Figure 3: Difference between measured and certified DIC values of measured CRMs, VINDTA A.

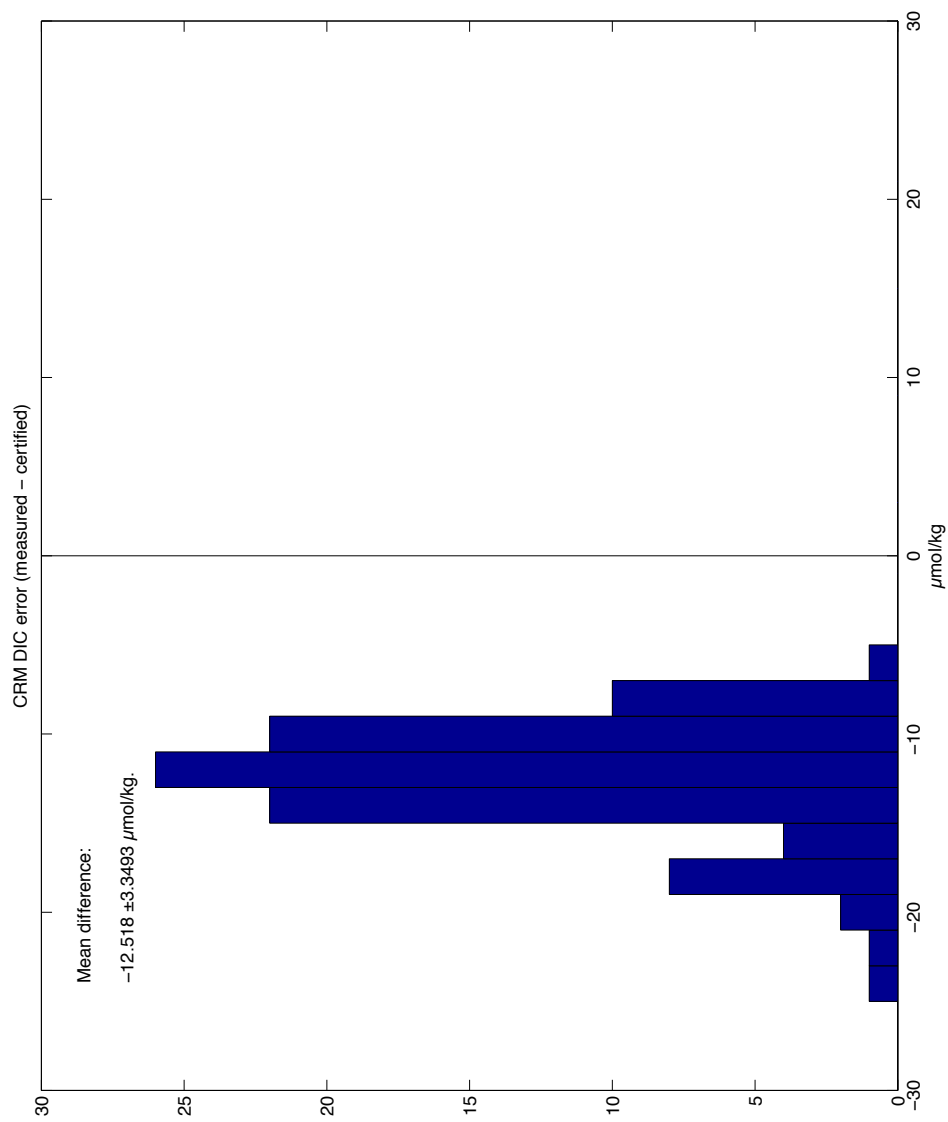


Figure 4: Difference between measured and certified DIC values of measured CRMs, VINDTA B.

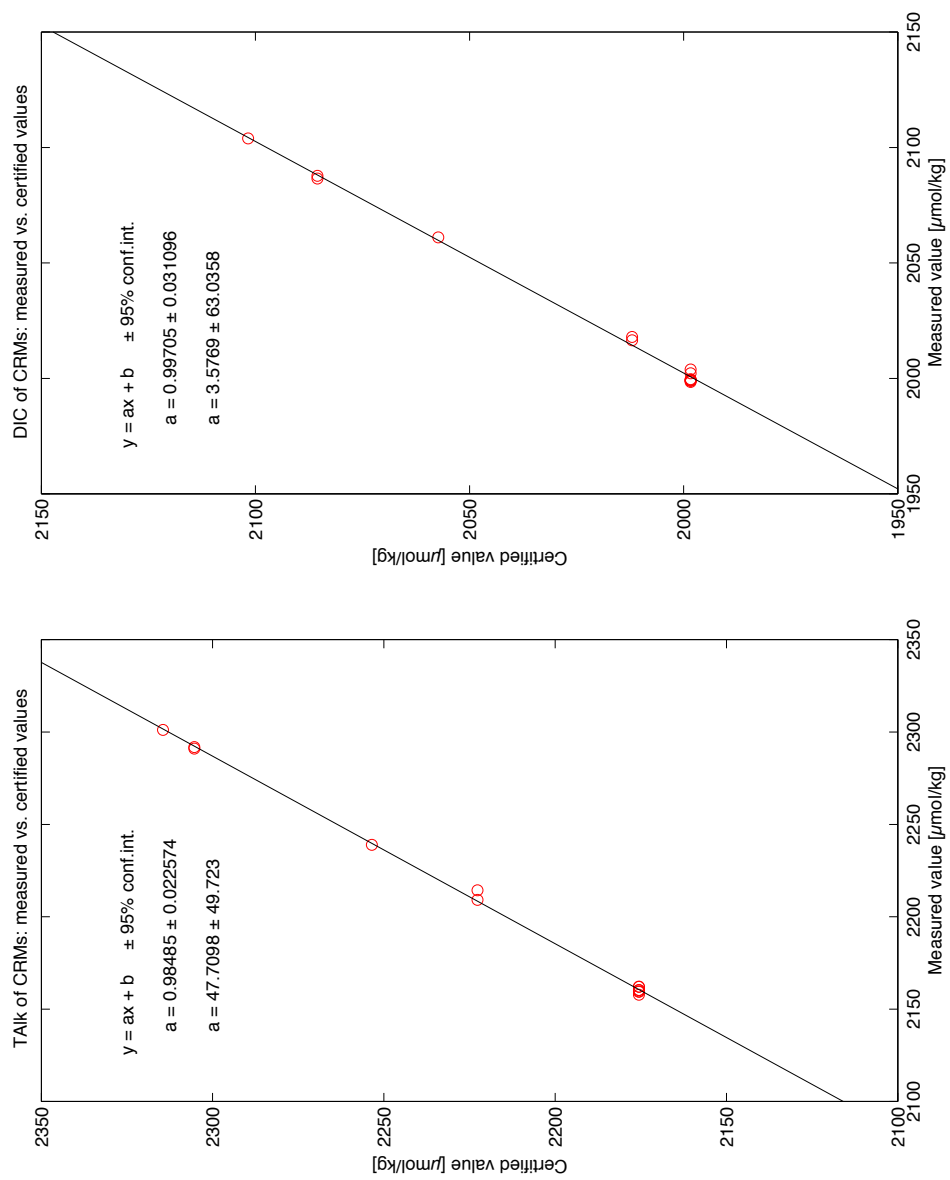


Figure 5: Regression between measured and certified values of a range of CRMs, VINDTA A.

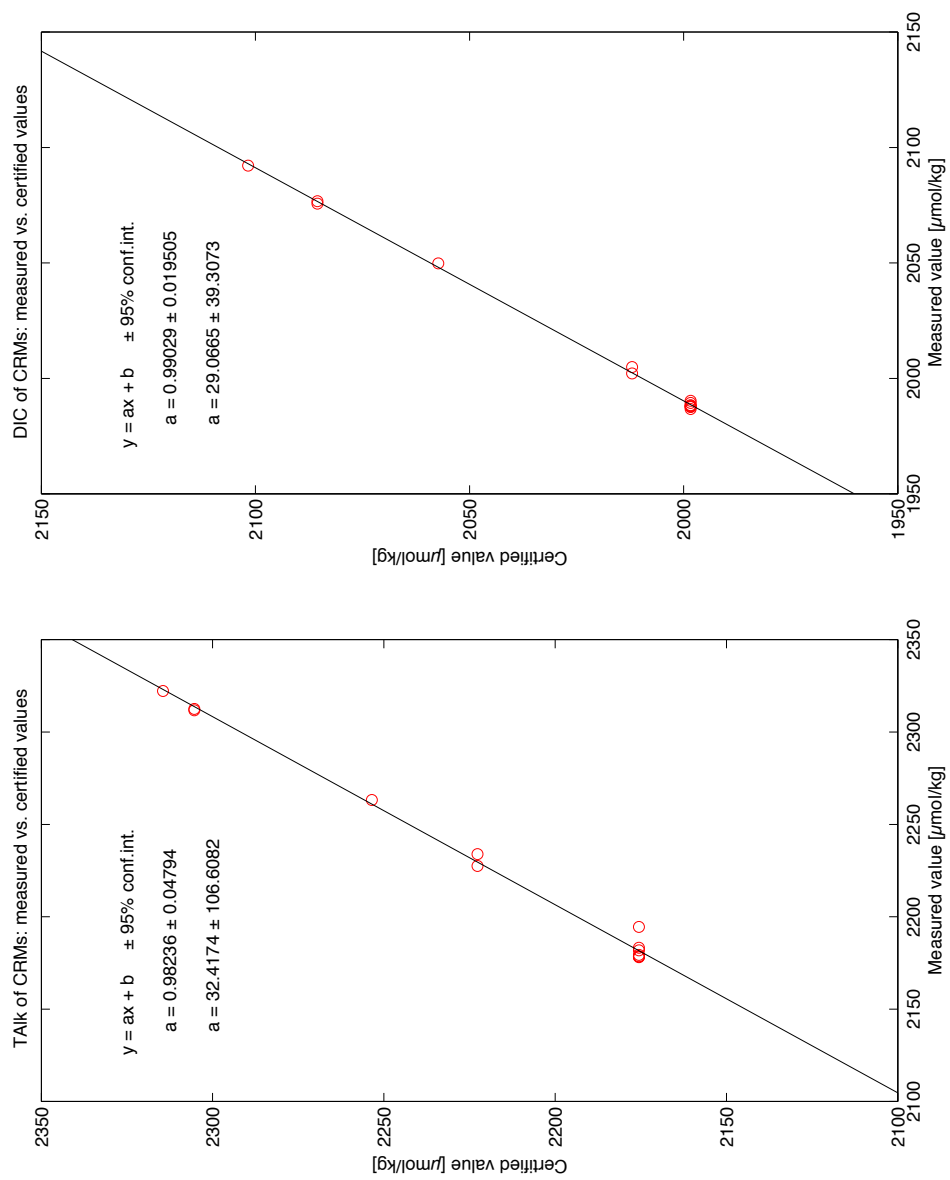


Figure 6: Regression between measured and certified values of a range of CRMs, VINDTA B.

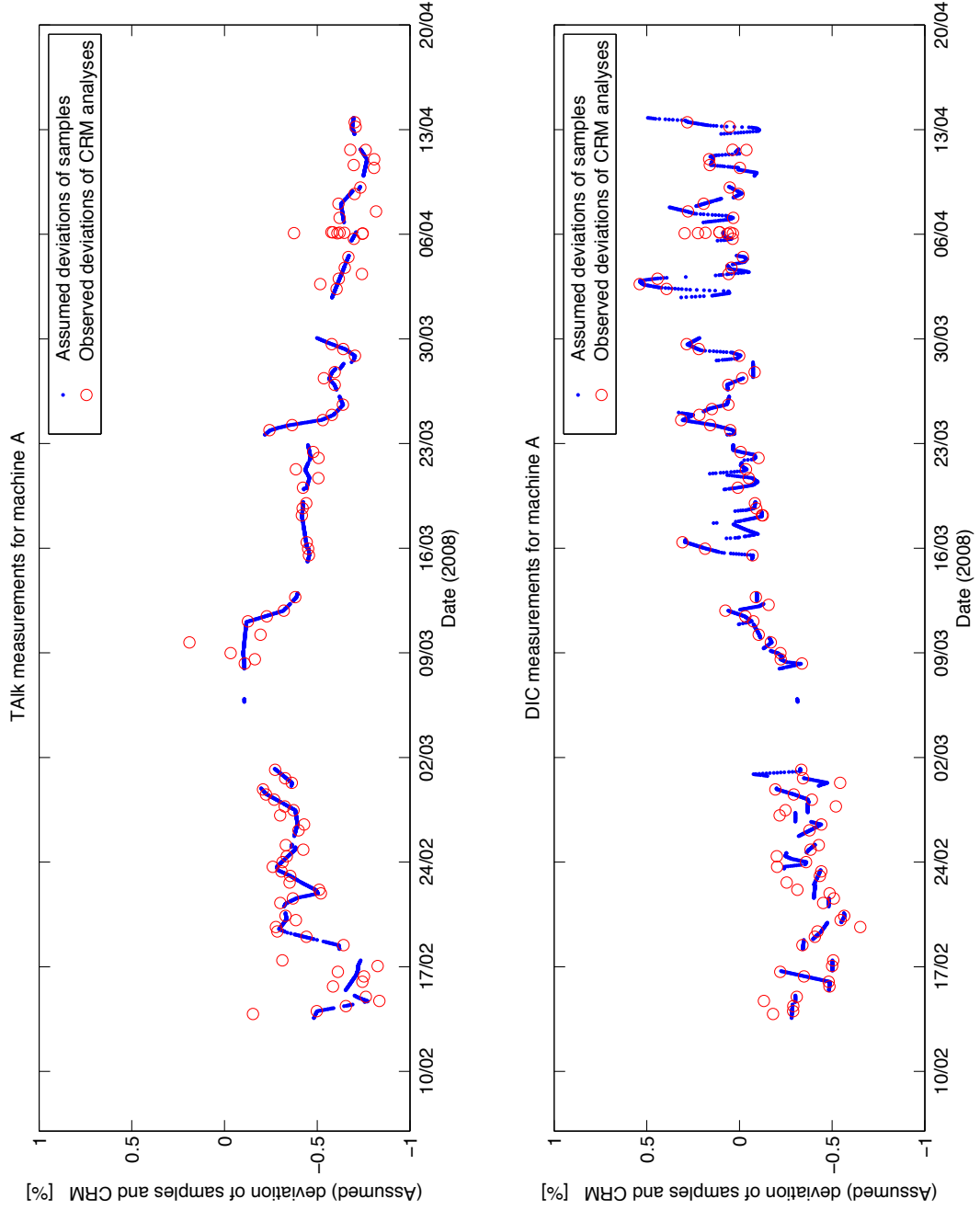


Figure 7: Timeseries of TALK and DIC CRM deviations and user-set correction factors, VINDTA A

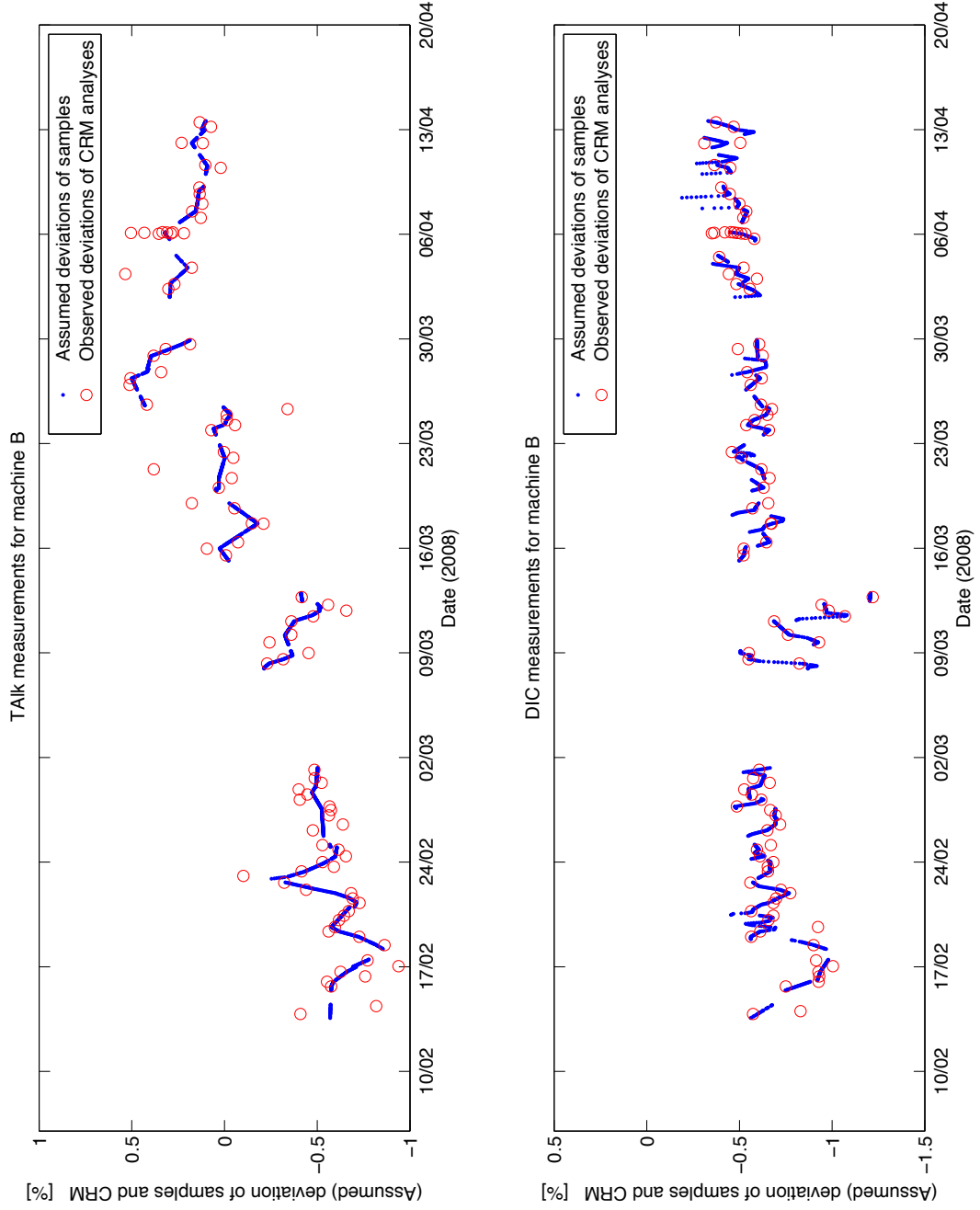


Figure 8: Timeseries of TALK and DIC CRM deviations and user-set correction factors, VINDTA B

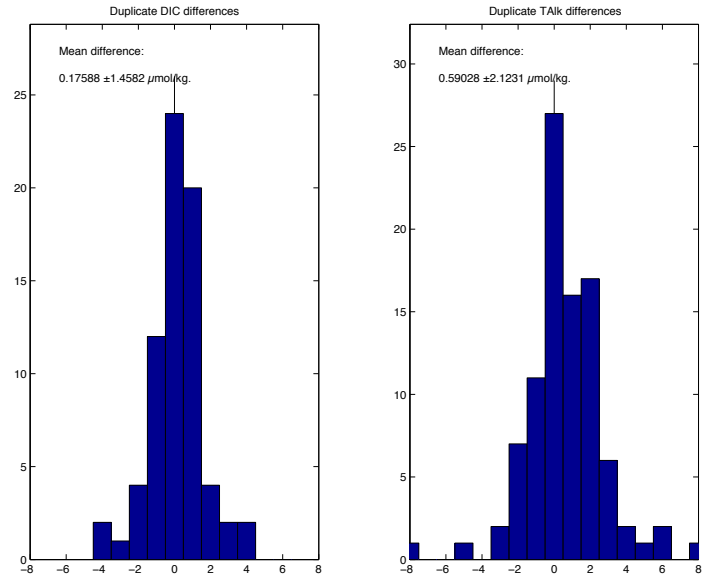


Figure 9: Histogram of differences between back-to-back duplicate analyses, VINDTA A.

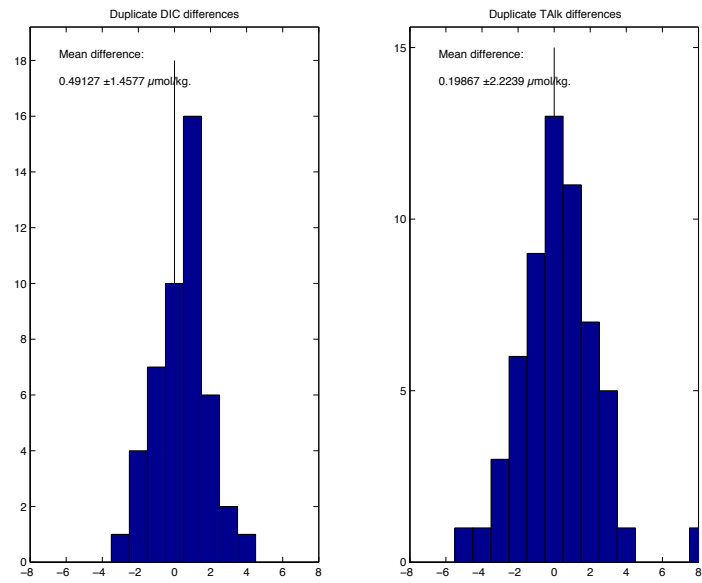


Figure 10: Histogram of differences between back-to-back duplicate analyses, VINDTA B.

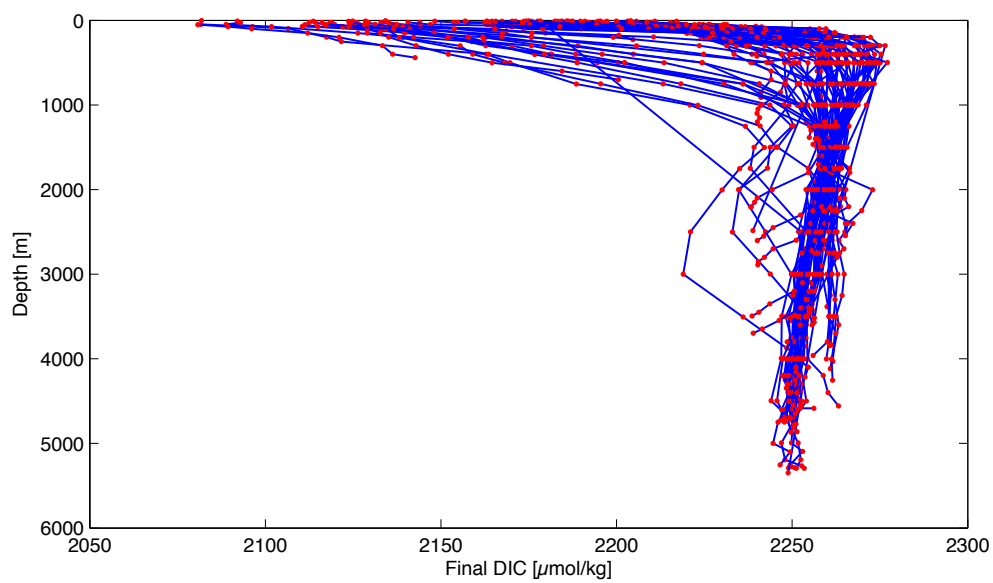
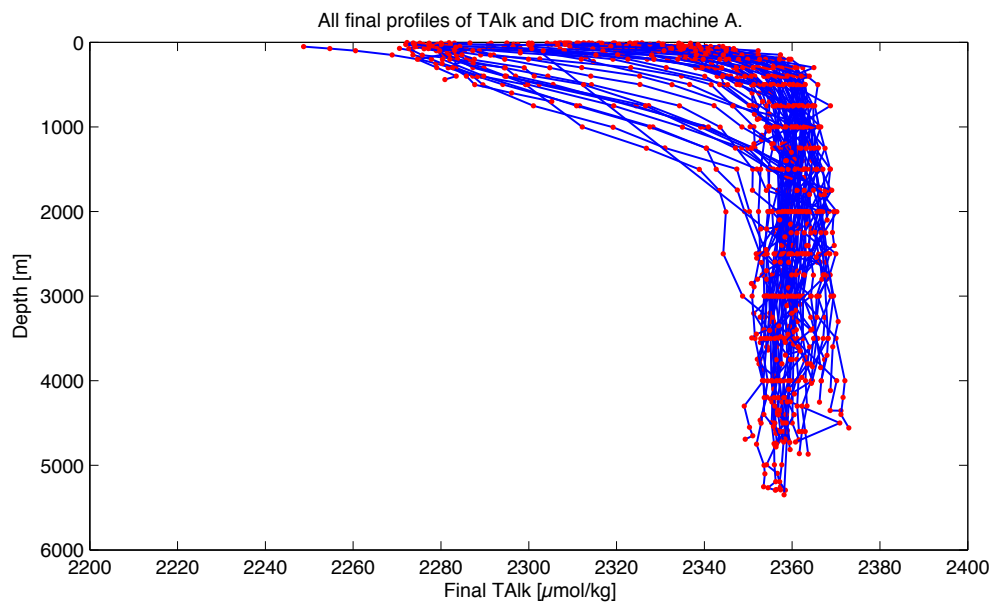


Figure 11: Depth profiles of final data for TALK and DIC, VINDTA A

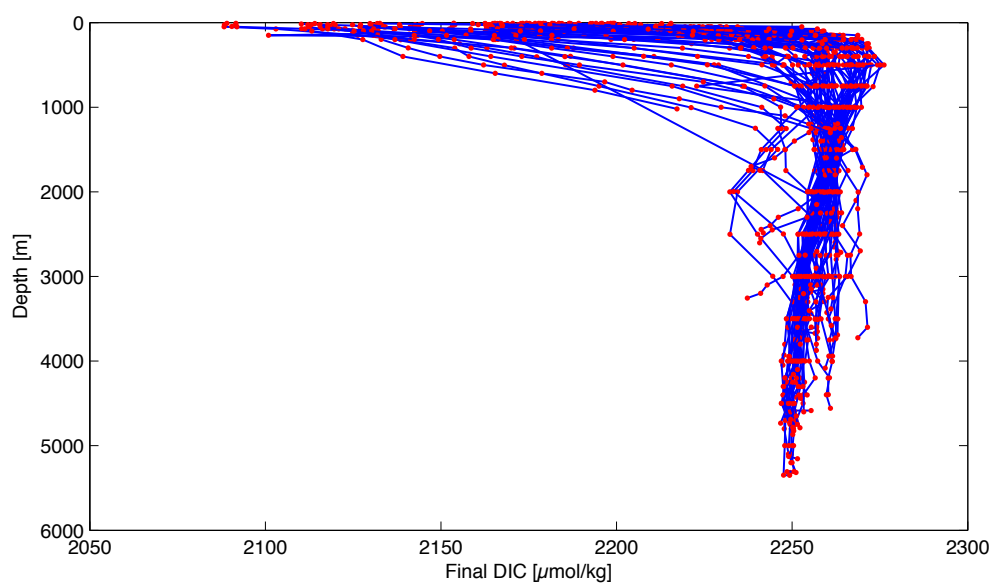
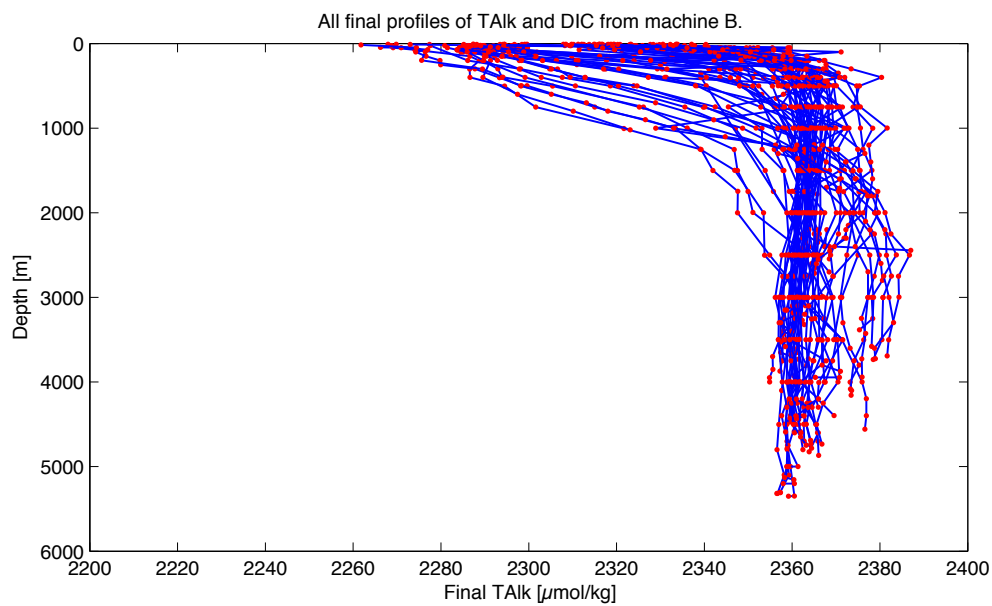


Figure 12: Depth profiles of final data for TALK (discarded...) and DIC, VINDTA B

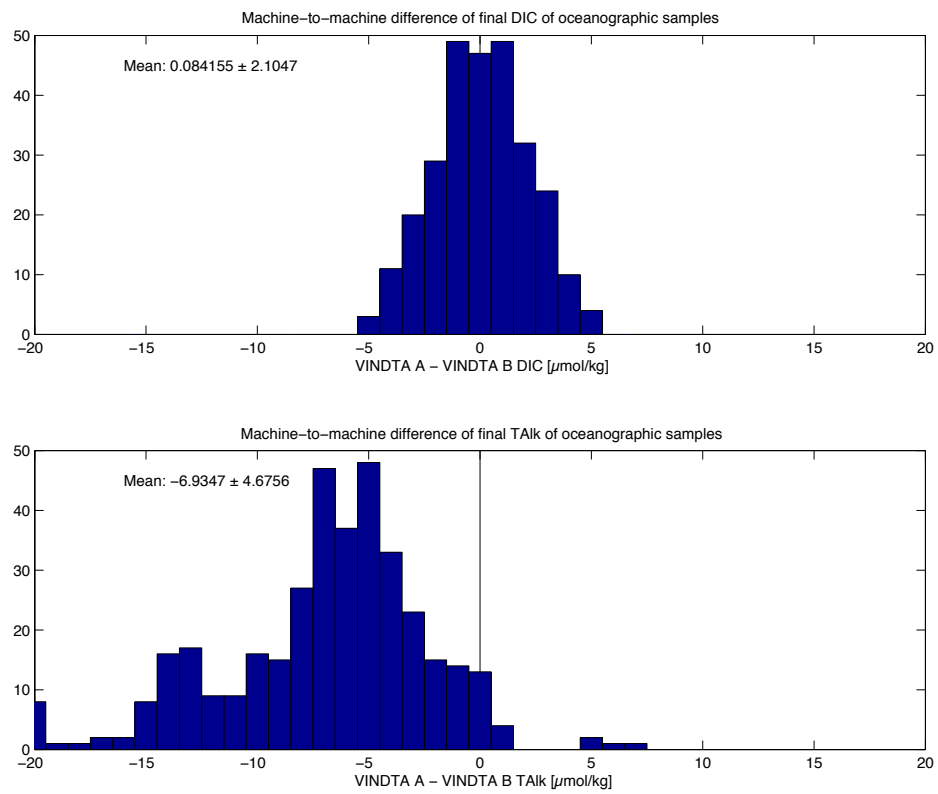


Figure 13: Histogram of differences between results of VINDTA A and VINDTA B (as A-B).

extracted from:

Fahrbach, E., de Baar, H.J.W. (Eds), 2010. The expedition of the research vessel "Polarstern" to the Antarctic in 2008 (ANT-XXIV/3). Reports on Polar and Marine Research 606, 232pp. [hdl:10013/epic.34050](https://hdl.handle.net/10013/epic.34050)

2.5 Oxygen measurements

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Oxygen measurements from samples

To calibrate the oxygen profiles measured with the optode sensor of both CTDs, from AWI and NIOZ, water samples of the Niskin bottles of both CTDs were taken from

station 97 to station 251. One sample of water was taken at the surface, one at the ocean bottom and one at the oxygen minimum. Additional samples were taken along the water column: one sample each thousand meters. In most of the cases, 5 or 6 water samples were taken from each cast. In shallow stations only 2 or 3 samples were taken. Every sixth CTD cast, replicas were taken (i.e., at least 15 % of the all the samples are replicas). In total, 651 samples were taken.

The oxygen was measured using the Winkler method, according to the manual "WOCE operation and methods" (C.H. Culberson, July, 1991). Immediately after the sampling, the dissolved oxygen was fixed with 1 ml of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 1 ml of $\text{NaOH} + \text{NaI}$. Then, the bottles were stored under water and their caps were attached with a rubber band to prevent intrusion of air. To measure the dissolved oxygen, 1 ml of Sulphuric Acid 50 % (H_2SO_4) was added to the samples and a solution of Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) was titrated with a Dosimat Metrohm automatic pipette provided with a transmissiometer. Potassium iodate (KIO_3) was used as standard. Preliminary results of these measurements show an accuracy of 0.028 ml l^{-1} (based on the standard deviation of 22 replicas).

While the AWI CTD sensor seems to be relatively stable (constant offset), the NIOZ CTD sensor drifted with time, measuring less oxygen every day, see Fig. 2.29. Due to problems with the Dosimat (failure of the device to measure some samples, bubbles in the pipette, etc.), the first half of the expedition (up to 10 March, i.e., station 163) results of the titration were not completely satisfactory: imprecise outcome of the titration resulted in a large dispersion of the offset around a straight line. After various attempts of improving the measuring process, on 10 March, the titer bottle and the pipette were changed; new titer was prepared, added to the bottle and standardized. After this, the titration results matched the CTD profiles along the vertical considerably better.

Monitoring of the offset between CTD and titration results ruled the sampling frequency of each CTD, depending on the dispersion of the off-set around the straight line. Because of this, the first half of the expedition, samples were taken from every cast of both CTDs. After the offset seemed to be stable, and considering that the AWI CTDs occurred with a large frequency, samples were taken only from one cast per day. Since casts of the NIOZ CTD occurred every second or third day, every cast of the NIOZ CTD has been sampled.

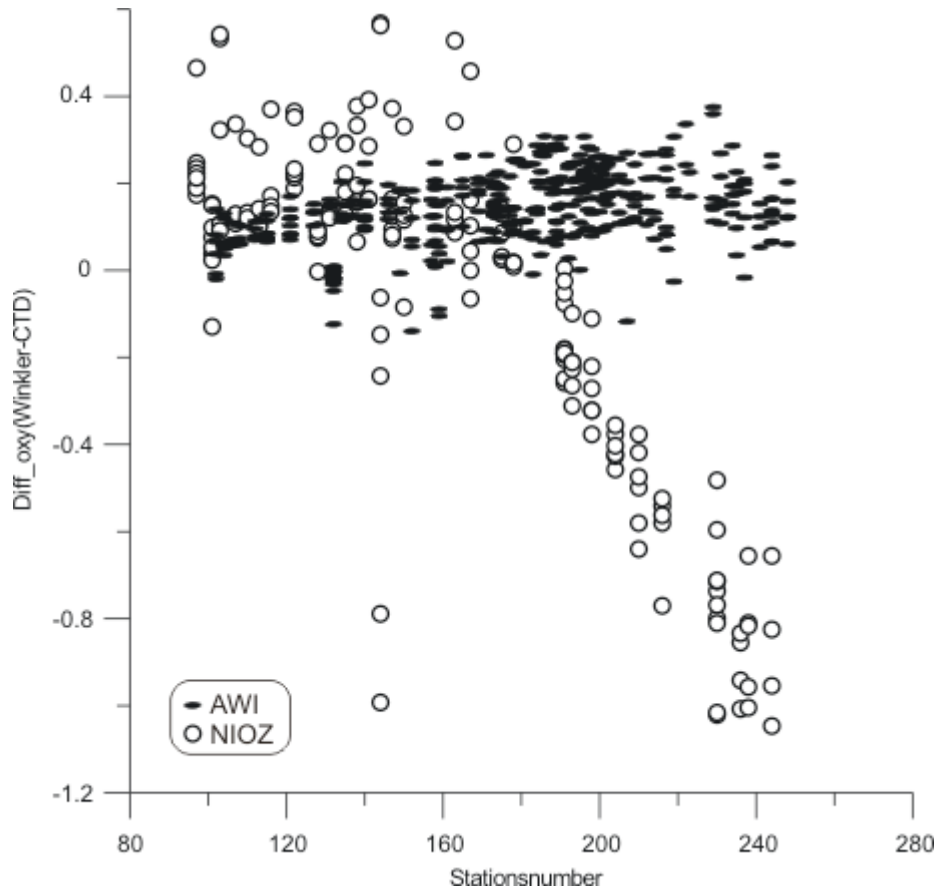


Fig. 2.29: Oxygen difference between the measured samples and the reading from the CTD's oxygen sensor versus station number for the AWI and NIOZ system

Three individual steps of correction were applied for the AWI CTD oxygen sensor:

1. Step: Linear correction of the CTD oxygen reading

$$OX\ Y1 = a + b * OX\ Y$$

with:

$$a = -0.02291300577$$

$$b = 1.029883905$$

2. Step: Linear correction of the oxygen sensor drifts

$$\Delta OX\ Y1 = a + b * Stationnumber$$

with:

$$a = -0.14125$$

$$b = 0.0008125$$

$$OX\ Y2 = OX\ Y1 + \Delta OX\ Y1$$

3. Step: High order polynomial fit to correct the pressure effect of the oxygen sensor

a: In upper water column; 0 to 2370 dbar:

$$\Delta OX\ Y2 = a + b * PRES$$

with:

$$a = -0.04598245614$$

$$b = 2.336842105E-005$$

and pressure given in decibar.

b: In the deep water column; pressure > 2370 dbar:

$$\Delta OXY_2 = a + b * PRES + c * PRES^2 + d * PRES^3 + e * PRES^4 + f * PRES^5 + g * PRES^6$$

with:

$$a = 0.01938375746$$

$$b = -0.0001436734808$$

$$c = 7.707321788E-008$$

$$d = 1.241336138E-011$$

$$e = -1.460247804E-014$$

$$f = 3.065354609E-018$$

$$g = -2.023542164E-022$$

and pressure given in decibar.

The final corrected CTD oxygen reading is:

$$OXY_{corr} = OXY_2 + \Delta OXY_2$$

The correction of the NIOZ CTD oxygen sensor was made for two separated parts due to the sensor drift which can be clearly identified in Fig. 2.29. Two individual steps of correction were applied for the first part from station number 97 to 178:

1. Step: Correction of the oxygen sensors pressure effect

$$\Delta OXY_1 = a + b * \log(\text{pressure})$$

with:

$$a = 0.5972460117$$

$$b = -0.05964890171$$

and pressure given in decibar.

2. Step: Linear correction of the oxygen sensor drifts

$$\Delta OXY_2 = a + b * \text{Stationnumber}$$

with:

$$a = 0.242$$

$$b = -0.0019$$

The final corrected CTD oxygen reading for station 97 to 178 is:

$$OXY_{corr} = OXY + \Delta OXY_1 + \Delta OXY_2$$

The following correction was applied for the second part from station number 187 to 252:

1. Step: Linear correction of the oxygen sensor drifts

$$\Delta OXY1 = a + b * Stationnumber$$

with:

$$a = 2.975$$

$$b = -0.01625$$

2. Step: High order polynomial fit to correct the pressure effect of the oxygen sensor

$$\Delta OXY2 = a + b * PRES + c * PRES^2 + d * PRES^3 + e * PRES^4 + f * PRES^5 + g * PRES^6$$

with:

$$a = -0.1744698393$$

$$b = 0.0007819713073$$

$$c = -8.445337449E-007$$

$$d = 3.882443376E-010$$

$$e = -9.007417652E-014$$

$$f = 1.034638749E-017$$

$$g = -4.679330148E-022$$

and pressure given in decibar.

The final corrected CTD oxygen reading for station 187 to 252 is:

$$OXY_{corr} = OXY + \Delta OXY1 + \Delta OXY2$$

Fig. 2.30 shows the remaining oxygen difference between the measured samples and the corrected reading from the CTD oxygen sensor. The sensor from the NIOZ CTD shows a little higher noise than the AWI CTD oxygen sensor which reflects the sensor problems which were already visible in the plot of the uncorrected data.

The standard deviation for the AWI CTD is 0.04 and 0.07 for the NIOZ CTD. From there the accuracy for all CTD oxygen is better than ± 0.1 ml/l.

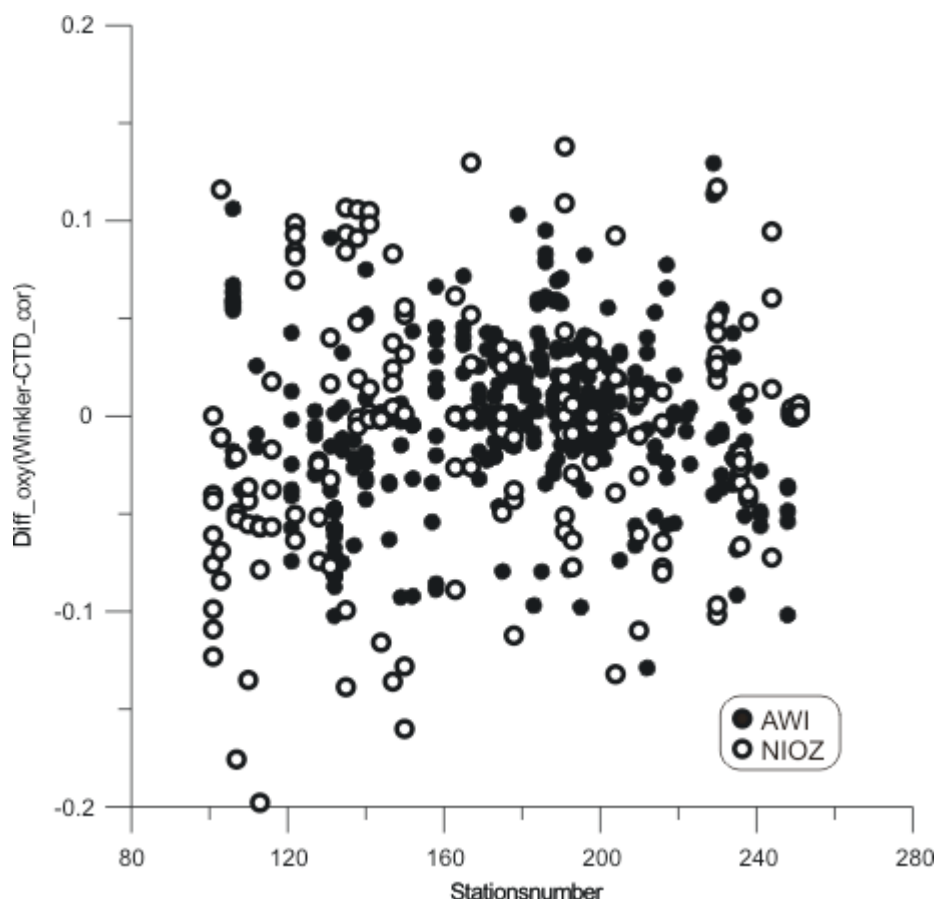


Fig. 2.30: Oxygen difference between the measured samples and the reading from the CTD's oxygen sensor after applied corrections versus station number for the AWI and NIOZ system.

The oxygen profiles of the CTD were constantly compared with the results of the titration along the expedition. The profiles were roughly corrected by shifting them horizontally (adding or subtracting an offset) until they optimally matched the titration results by minimal quadratic differences (Fig. 2.31 shows station 244 as an example). Fig. 2.32 shows the offset between each CTD profile and the corresponding titration values against the station number.

The authors of this report wrote also an succinct manual about oxygen sampling and measuring. This manual is available under request.

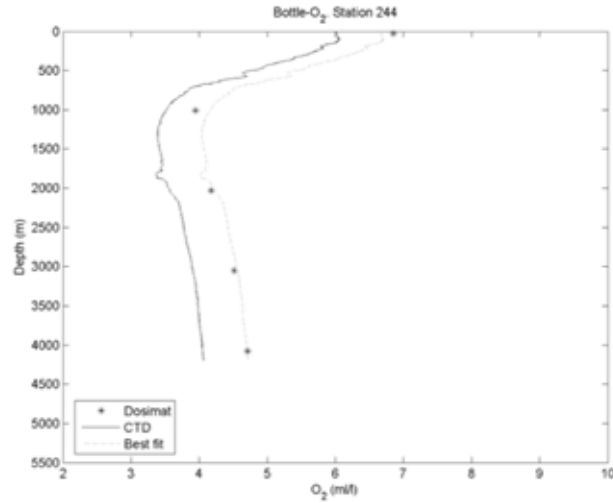


Fig. 2.31: Comparison of the oxygen profile of the CTD sensor of Station 244 (black continuous line) and the titration values (stars). To monitor the results (and not as calibration procedure), the CTD profile has been shifted adding an offset until it matched by minimum quadratic differences the titration values (grey dashed line).

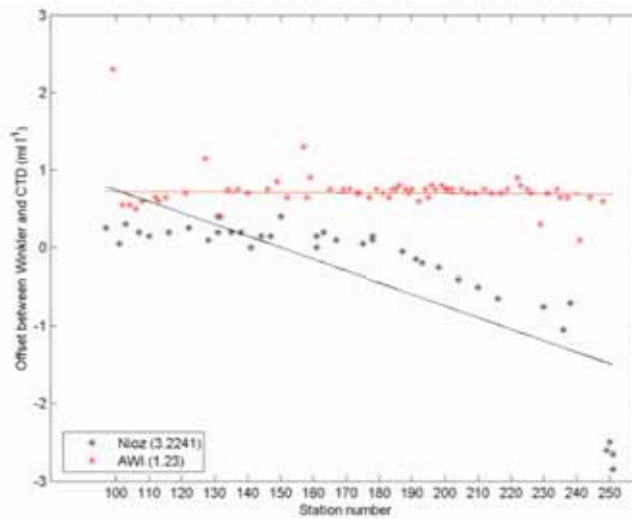


Fig. 2.32: Offset between the CTD oxygen profiles and the titration results for the AWI CTD (red) and the NIOZ CTD (black) as a function of the station number. The offset is defined as the amount of oxygen added or subtracted to the profile as to match the titration values by minimum quadratic differences.

extracted from:

Fahrbach, E., de Baar, H.J.W. (Eds), 2010. The expedition of the research vessel "Polarstern" to the Antarctic in 2008 (ANT-XXIV/3). Reports on Polar and Marine Research 606, 232pp. [hdl:10013/epic.34050](https://hdl.handle.net/10013/epic.34050)

3.4 Nutrient measurements during ANT-XXIV/3

Jan van Ooijen
NIOZ

Background

On this cruise samples were analysed on phosphate, silicate, nitrate and nitrite. At the end of the cruise there will be about 18,000 analysis (4,500 samples) accomplished on a Bran and Luebbe Traacs800 Autoanalyser connected to an autosampler. The different nutrients were determined colorimetrically as described by Grashoff (1983).

Methods

Samples were obtained from a CTD rosette sampler, an ultraclean CTD and of algae growth experiments. All samples were obtained in a polyethylene vial and the samples of the algae growth experiment were filtered over a 0.20 µm acrodisc filter. They were all stored dark at 4°C. CTD samples were analysed within 12 hours all other samples within 24 hours on a Technicon TrAAcs 800 autoanalyzer.

Standards were prepared fresh every day by diluting the stock solutions of the different nutrients in nutrient depleted surface ocean water. This water is also used as baseline water. Each run of the system had a correlation coefficient for 9 calibrant points of at least 0.9999. The samples were measured from the lowest to the highest concentration in order to keep the carry over effects as small as possible.

In every run a mixed nutrient standard containing silicate, phosphate and nitrate in a constant and well known concentration, a so called antarctic nutrient-cocktail, was measured in duplicate. This cocktail is used as a guide to check the performance of the analysis and used to make a correction at the end of a transect obtaining the final data.

Over the last 20 years this cocktail has proven to be stable for at least 10 years and has also been used and monitored in many intercomparison tests (ICES, Quasimeme). The reduction efficiency of the cadmium column on the NO_x manifold was at least 97 % and measured in each run.

Chemistry

Silicate reacts with ammoniummolybdate to a yellow complex, after reduction with ascorbic acid the obtained blue silica-molybdenum complex was measured at 800 nm. Oxalic acid was used to prevent formation of the blue phosphate-molybdenum.

Phosphate reacts with ammoniummolybdate at pH 1.0, and potassiumantimonyl-tartrate was used as an inhibitor. The yellow phosphate-molybdenum complex was reduced by ascorbic acid and measured at 880 nm.

Nitrate plus nitrite (NO_x) was mixed with a buffer imidazol at pH 7.5 and reduced by a copperized cadmium column to nitrite. This was diazotated with sulphonylamide and naphthylethylenediamine to a pink colored complex and measured at 550 nm.

After subtracting the nitrite value of the nitrite channel the nitrate value was achieved.

Nitrite was diazotated with sulphonylamide and naphthylethylenediamine to a pink colored complex and measured at 550 nm.

Statistics after corrections for the Greenwich meridian transect

The standard deviation of reference material within a run:

PO ₄ :	0.006 uM	0.16 % of full scale value
Si :	0.084 uM	0.06 % of full scale value
NO _x :	0.063 uM	0.13 % of full scale value
NO ₂ :	0.001 uM	0.05 % of full scale value

The standard deviation of reference material between the runs are:

PO ₄ :	0.009 uM	0.27 % of full scale value
Si :	0.464 uM	0.33 % of full scale value
NO _x :	0.222 uM	0.24 % of full scale value
NO ₂ :	0.006 uM	0.39 % of full scale value

Suspicious bottles

Bottles which seem not to have closed at the right depth at the Greenwich meridian transect are:

CTD 106-1-1
CTD 127-1-2
CTD 134-1-4 or CTD 134-1-1

Preliminary results

An overlook of the results of the nutrient analysis on the Greenwich meridian transect is plotted in ODV (Fig. 3.33).

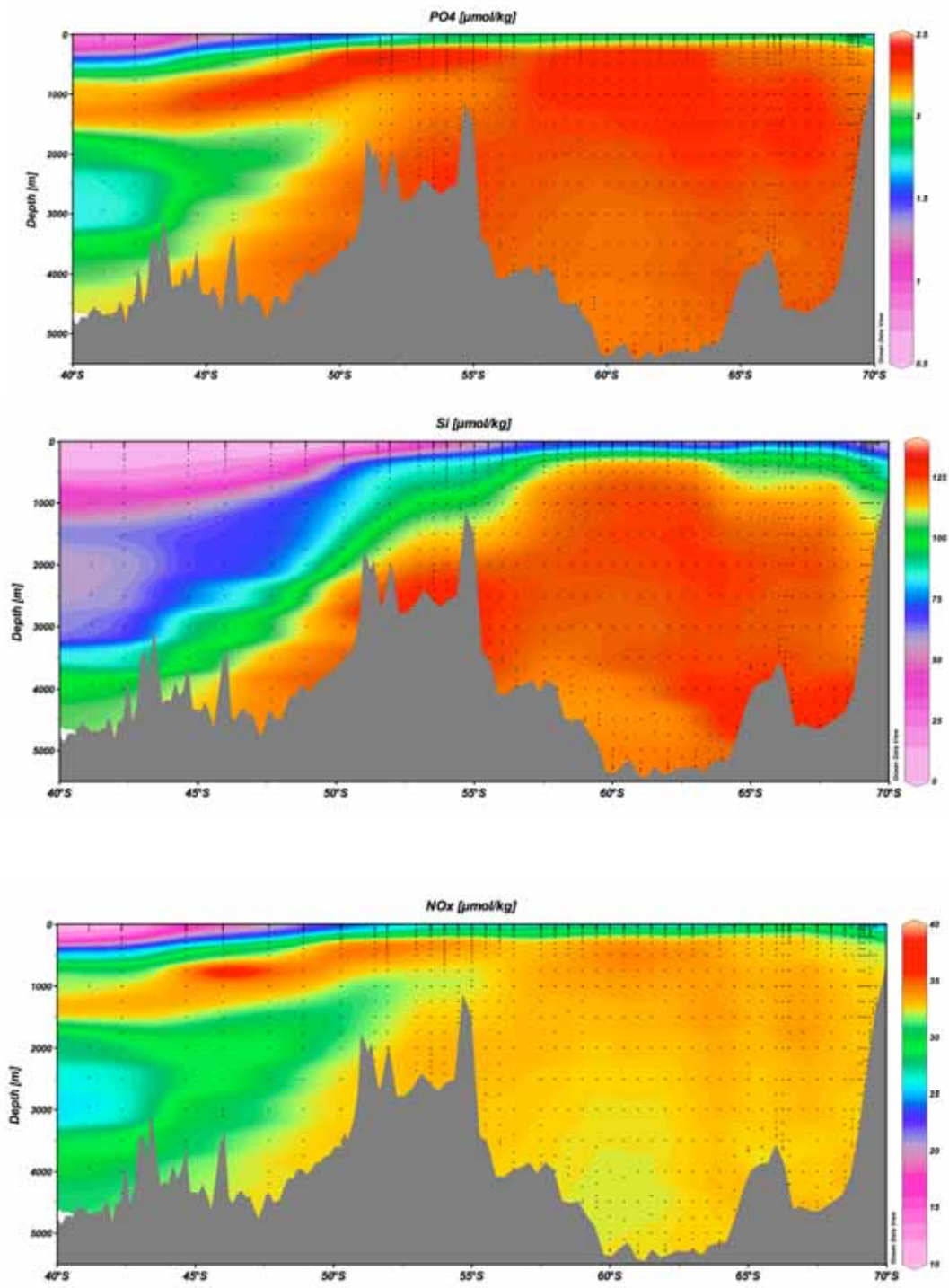


Fig. 3.33: Vertical transects of Si and NO_x along the Greenwich meridian